Seasonal Deposition Fluxes of Polycyclic Aromatic Hydrocarbons (PAHs) in Lake Biwa, Japan

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Seasonal deposition fluxes of Polycyclic Aromatic Hydrocarbons (PAHs) in Lake Biwa, Japan

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Abstract

Seasonal deposition fluxes of polycyclic aromatic hydrocarbons (PAHs) in the North Basin of Lake Biwa were investigated by monthly collecting sediment trap samples through a year from July 2003. Average deposition flux of total PAHs was 75 ng cm^{-2} $year^{-1}$, similar to those for other rural area. Deposition fluxes of PAHs did varied seasonally. In the vertical mixing period of the lake, late autumn to early spring, the fluxes of less volatile PAHs were enhanced while those for volatile PAHs were not. The size difference of particles associated with volatile and less volatile PAHs caused the seasonal variation of the fluxes. Oil discharge from water delivery equipments may contribute the fluxes of volatile PAHs in summer to autumn.

Key words

PAH; Lake Biwa; deposition flux; sediment trap; seasonal variation

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are one of the classes of organic compounds that have two or more fused benzene rings. The more the rings the PAHs have, the less volatile and less soluble the PAHs are. Although PAHs occur naturally, high levels of them are emitted by combustion process by cars, trucks, wood burning, coal fired plant, and waste incinerators in both gas and aerosol phase (Khalili et al, 1995; Venkataraman et al., 1999; Yamasaki et al., 1982). PAHs are also concentrated in petroleum, lubricants and crank case oil (Kimbrough and Dickhut, 2006), and leakage of them results in PAHs contamination in the environment. In the past, ubiquitous presence of PAHs has been revealed in the atmosphere, natural water, soil, and sediment (Fernandez et al., 2002; Halsall et al., 1997; Laflamme and Hites, 1977; Mielke et al., 2001; Zhou and Maskaoui, 2003).

Some PAHs and their derivatives are mutagenic and carcinogenic (Atkinson and Arey, 1994; Kennaway, 1955; Nielsen et al., 1983), being included in the USEPA and EU priority pollutants lists. The fate of PAHs after released in the environment has been concerned intensively with adverse effect on living creatures in mind. Lake sediment serve as one of the major repositories of PAHs and their concentration and distribution have been investigated in many locations. Particularly, past and present deposition fluxes of PAHs into lake sediment has been revealed and related to the emission intensity of PAHs by human activities (Gschwend and Hites, 1981; Su et al., 1998; Wakeham et al., 1980) and adverse effects on aquatic organisms (Boxall and Maltby, 1997). However, seasonal variation of the deposition fluxes of PAHs and their variation mechanisms have rarely been clarified.

Lake Biwa, largest lake in Japan, serves as drinking water resource for about 14 million people along the watershed of rivers from the lake. The environmental pollution of the lake has been investigated by many researchers in various aspects (e.g. Ichiki et al., 1998; Ichiki and Yamada, 1999; Kobayashi et al., 1975; Naito et al., 2002). On the other hand, the deposition fluxes of PAHs have not been investigated yet which may change seasonally according to seasonal emission intensity of PAHs, seasonal state of the lake, and physicochemical characteristics of the individual PAH.

In this context, the purposes of this study are (1) to reveal accurate deposition fluxes of PAHs in Lake Biwa, and (2) to clarify seasonal variation of the deposition fluxes of them. We collected sediment trap samples monthly through a year from July 2003. The sediment trap samples were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), total organic carbon (TOC) and particle size analyses to reveal the seasonal variation mechanisms of the PAHs fluxes.

Materials and Methods

Lake Biwa is divided into the South and North Basin according to the geomorphology (**Fig. 1**). The surface area of the lake is 674 km^2 (58 km^2 for South, 616 km^2 for North) and the averaged depth for the South and North Basin are respectively 4 m and 43 m with the deepest part being 103.6m in the North Basin.

Sediment traps were set in the North Basin of Lake Biwa (35°N19.9, 136°E07, **Fig. 1**) above 5 m from the bottom surface of the lake. The depth from the surface water to the sediment trap was about 95 m. The biggest river flowing into the lake near the sampling point is the Ado River (**Fig. 1**) whose drainage area and length are 311 km^2 and 52 km, respectively. Rural town (called Takashima city, with a population and area of 55

thousands and 510 km^2 respectively) is located along the river. The land is mainly used as rice fields and the major national street runs along the west margin of the lake near the sampling location.

The sediment trap was made by tightly connected two vinyl chloride cylinders with bottom end closed by a vinyl chloride cover. The entrance of the sediment trap was covered by vinyl net with opening aperture 3 mm. Vertical lengths and diameter of the cylinder was 50 cm and 10 cm, respectively.

Sediment trap samples were collected monthly from July 2003 through a year (Table 1). After drawing up the sediment trap from the lake, the samples were separated from lake water by centrifugation (3000×g for 40 min.) and freeze dried. The dried samples were stored in a refrigerator (4 □) before analysis. Surface sediment samples of the lake (0.4 cm from the top of the surface) near the sediment trap location was also taken in February 14, 2007 and freeze dried. The dried samples were stored in the refrigerator prior to analysis.

Mean particle size of the sediment trap samples was calculated after analyzing size distribution of the samples by a laser diffraction dispersion method (SHIMADZU, SALD 2000-J). The morphological and chemical characteristics of the sediment trap samples were revealed by SEM (JEOL JSM-5600) imaging operated at 25.0 kV in conjunction with energy dispersive X-ray spectrometry (EDS; Oxford Microanalysis Group EDS Link Isis).

TOC of the sediment trap samples was measured by a TOC analyzer (SHIMADZU, TOC-5000) equipped with a solid sample combustor (SHIMADZU, SSM-5000A). The accuracy and standard deviation of the measurements were tested using lake sediment reference materials (CANMET, LKSD-2). Standard deviation of the measurement was 0.12 % and the discrepancy between standard and average measured values was 0.68 %. Mineral composition of each sediment trap sample was determined by XRD on a Rigaku powder diffractometer using monochromatic CuKα radiation operated at 40 kV and 30 mA. Precipitation amounts during the sampling intervals were calculated from the data provided by the national meteorological observatory (at Imazu), nearest from the sampling location.

Prior to PAHs extraction, the samples were spiked with five deuterated PAH internal standards: Nap-d_{10}, Ace-d_{10}, Phe-d_{10}, Pyr-d_{10}, and Bap-d_{10}. The extraction procedure of PAHs was followed by Hayakawa's method as follows: each sample was immersed with excess amount of benzene/ethanol (3:1,v/v) and ultrasonically agitated twice for 20 minutes. The extracts were concentrated to about 0.5 ml by a rotary evaporator at low temperature (T＜36 ℃). The concentrated extracts were redissolved by adding 0.8ml of acetonitrile and stored for subsequent high performance liquid chromatography (HPLC) analysis. PAHs were separated on an Inertsil ODS-P (4.6 i.d.×250 mm) separation column (GL SCIENCE) with 50:50 acetonitrile/water-100 % acetonitrile gradient, run over 90 min at a flow rate of 1 mL/min. The gradient was produced by dual pumps (THOSO, DP-8020), and detection was by a fluorescence detector (SHISEIDO, NANOSPACE SI-2). The quantified PAHs (with their abbreviations) and used excitation/emission wavelengths (nm) by the fluorescence detector were as follows: Fluorene (Flu, 286/433), Phenanthrene (Phe, 280/340), Anthracene (Ant, 250/400), Benzo[a]anthracene (BaA, 264/407), Chrysene (Chr, 264/407), Benzo[k]fluoranthene (BkF, 264/407), Benzo[a]pyrene (BaP, 264/407), Benzo[g,h,i]perylene (BghiP, 264/407). Relative standard deviations of the measurements were less than 0.13 tested by spiked PAH standards. Average recoveries for each spiked PAH standards ranged 50-80 %.

Results and discussions

Deposition fluxes of the particles

Seasonal deposition fluxes of the particles with the precipitation amount are shown in **Fig. 2**. The prominent increment of the flux (12.3 mg cm^{-2} 30 $days^{-1}$) was recognized in August 2003. The increasing trend of the deposition fluxes was observed from December 2003 (6.00 mg cm^{-2} 30 $days^{-1}$) to April 2004 (13.8 mg cm^{-2} 30 $days^{-1}$) followed by the sudden drop of the flux in May 2004.

The high deposition flux observed in August 2003 would be caused by the typhoon No 10 hit around the sampling location from August 7 to 10, 2003. The high deposition fluxes from December to April regardless of low precipitation amount were caused by the "vertical mixing" of the lake, described below. From spring to late autumn, the North Basin of Lake Biwa is thermally stratified forming a themocline (Kumagai et al., 1987), above which warmed epilimnion tends to remain there (which gets lighter than hypolimnion below). From late autumn to early spring, the thermocline is destroyed by cooled eplimion that sinks downward called "vertical mixing" in the lake (Aota et al., 2006; Inouchi, 1990).

Seasonal characteristics of the sediment trap samples

Fig. 3 shows mean particle size of the sediment trap samples. The mean particle size is comparably large (9-12 μm in diameter) during October to December 2003, and tended to decrease until April 2004 (3.3 μm in diameter). The SEM observations of the sediment trap samples showed the existence of crustal materials (whose major chemical composition is Si, Al, Mg and O), diatom cells and other materials (organic matter etc.). The marked enrichment of diatom cells was observed in the samples collected from January to May 2004 (**Fig. 4a, 4b**). Carbon content was not detected in the diatom cells suggesting decomposition of the organic components along their course of deposition (Soumiya et al., 2000). TOC (%) in the sediment trap samples increased from September to its highest value (11.03 %) in November 2003 (**Fig. 5**). The TOC continuously decreased from this month until its lowest value (4.06 %) in April 2004, and increased again until the end of the sampling period (July 2004) (**Fig. 5**). XRD analyses for the sediment trap samples show that the mineral components of the sample are consisted from quartz, feldspar, kaolinite and mica for all seasons.

The decreasing trend of the mean particles size from December 2003 to April 2004 in the vertical mixing period (**Fig. 3**) would be explained by facilitated transportation of fine particles, including diatom cells to the bottom part of the lake. That is consistent with the decreasing trend of TOC in the corresponding period (**Fig. 5)** because of relative enrichment of siliceous diatom cells in the samples. **Fig. 6** shows the peak intensity ratio of mica (at about 8.8° 2θ) over quartz (at about 26.6°2θ) in the XRD patterns. The higher the ratio is, the higher the content of mica relative to quartz in the sample. The marked feature was increasing trend of the ratio from January to its highest value in April 2004. The trend would also suggest facilitated transportation of fine particles in this period because clay minerals are comparably smaller than quartz (Moore and Reynolds, 1997).

The mean particles size, morphological characteristics, TOC, and mica/quartz ratio of the samples suggest that facilitated transportation of fine particles downward in the vertical mixing period.

Contents and deposition fluxes of PAHs in the sediment trap samples

As a general trend, PAHs contents in sediment and their fluxes are higher in urban/industrial area and

lower in rural/remote area. The comparison of the PAHs contents and fluxes with those by other studies should reveal the pollution level of PAHs in Lake Biwa with an outward-looking perspective. Table 2 shows the comparison of average PAHs contents (ng g^{-1}) in the sediment trap samples and the surface sediment collected with those in other studies. The PAHs contents are generally comparable to those in remote/rural or midsize city area. The average deposition flux of total PAHs (ng cm^{-2} $year^{-1}$) in this study was higher than that in remote lakes (Gschwend and Hites, 1981), comparable to that in rural area (Ikenaka et al., 2005), and lower than that near urban area (Bixian et al., 2001; Latimer and Quinn, 1996) (Table 3).

Seasonal deposition fluxes of PAHs in the sampling location are shown in **Fig. 7**. The relatively high values of the deposition fluxes of 3 rings PAHs were observed from August to November 2003 while deposition fluxes of 5-6 rings PAHs tended to be high from January to April 2004 in the vertical mixing period. The variation of the deposition fluxes of 4 rings PAHs seem to behave the intermediate between 3 and 5-6 rings PAHs. Giving attention to the August when particles deposition flux was high due to the typhoon event (**Fig. 2**), the deposition fluxes of 3-4 rings PAHs were relatively high (Flu and BaA marked their highest values) while those of 5-6 rings PAHs were not.

Seasonal variation mechanisms of the fluxes of PAHs

PAHs concentration associated with aerosol particles are generally high in winter and low in summer (Kaupp and McLachlan, 1999; Kiss et al., 2001; Tamamura et al., 2007; Tang et al., 2005). Such trend was not observed for the deposition fluxes of PAHs in the lake especially for volatile PAHs (3 rings). The simple atmospheric fallout of PAHs and their direct deposition into the lake sediment would not explain seasonal variation of the deposition fluxes of PAHs.

Atmospheric dry and wet deposition fluxes of total PAHs in the sampling region would be comparable to those at rural area for similar setting. We assume those fluxes in the sampling location comparable to those of Wolf Neck (a peninsula jutting about 4 km into Casco Bay) measured by Golomb et al. (2001). From their data, total atmospheric deposition flux of PAHs in the sampling location are estimated to be 30 ng cm^{-1} $year^{-1}$ (10 ng cm^{-1} $year^{-1}$ for dry and 20 ng cm^{-1} $year^{-1}$ for wet deposition, assuming annual precipitation amount of 1900 mm in our sampling location) which is less than the total deposition flux of PAHs (74 ng cm^{-2} $year^{-1}$ on average, Table 3) in the sampling location. Atmospheric deposition flux of PAHs would not solely compensate for the total deposition flux of PAHs in Lake Biwa. Terrestrial runoff particles (e.g. automobile exhaust, asphalt, tire particles, humic substances, crustal materials) must be considered as another source of PAHs (Hoffman et al., 1984; Su et al., 1998; Wakeham et al., 1980; Yang, 2000).

The aerosol particles are generally smaller than 10 μm (Mészáros, 1999), while runoff particles are usually in the size range from 50-2000 μm (Yang et al, 1999; Lee et al., 2005). Less volatile PAHs (5-6 rings) tend to distribute in pyrolytic aerosol particles (Ross and Oros, 2004; Lee et al., 2005). On the other hand, volatile PAHs (3 rings) tend to distribute not only in the (fine) aerosol particles, but also in (coarse) runoff particles (Hoffman et al., 1984; Lee et al., 2005; Takada et al., 1990; Venkataraman et al., 1999). Consistently, Simpson et al. (1998) and Oen et al., (2006) pointed out that less volatile PAHs tend to be enriched in fine particles while volatile PAHs tend to distribute in coarse particles in coastal sediment.

The mechanisms for coarser particles to be enriched in volatile PAHs include (1) While less volatile

PAHs tend to remain in the (originally sorbed) soot particles, volatile PAHs mainly distribute in gas phase and secondary sorb on coarser particles in the surface environment (Venkataraman et al., 1999) to be deposited as coastal sediment. (2) Street dust particles are generally coarser than aerosol particles and contain tar-like materials (Wakeham et al., 1980) which could be the source of Phenanthrene rich particles (Hoffman et al., 1984).

The increased deposition fluxes of less volatile PAHs in the vertical mixing period (**Fig. 7**) would be explained by facilitated transportation of (fine) aerosol particles which are enriched with less volatile PAHs. When thermocline is developed, coarse particles (which are enriched with volatile PAHs) would exclusively be deposited resulting in the relatively high fluxes of the volatile PAHs in the period (**Fig. 7**). In August 2003, enhanced deposition fluxes of 3-4 rings PAHs would be induced by the increased deposition flux of runoff particles due to the typhoon event in this month. In addition, discharge of oil (which is enriched with volatile PAHs (Wang et al., 1997; Wang et al., 2001)) from water delivery equipments such as cruise ships, personal water crafts and ferries (Davenport and Davenport, 2006) may contribute to enhance the deposition fluxes of volatile PAHs from summer to early autumn.

Phenanthrene and Anthracene are two structural isomers of which Phenanthrene is more thermodynamically stable compound than Anthracene. Phe/Ant ratio of sediment is used as source indicator of the PAHs with higher ratio suggesting petrogenic origin rather than pyrolytic aerosol origin (Tam et al, 2001; Yang, 2000). Reported values of Phe/Ant rations (Fang et al., 2004; Omar et al., 2002) are generally higher for runoff particles than ambient aerosols. Tarlike particles resembling asphalt (Wakeham et al., 1980) could be a reason of relative enrichment of Phe compared to Ant in runoff particles. **Fig. 8** illustrates seasonal Phe/Ant ratios of the sediment trap samples. The ratios tended to be lower in the vertical mixing period suggesting relative enrichment of pyrolytic aerosols in this period. This effect may also have been contributed by the contamination of oil-derived Phe (rather than pyrolytic Ant) in sediment trap samples discharged from the water delivery equipments from summer to early autumn.

Seasonal deposition fluxes of PAHs indicate that PAHs of any origins are deposited as lake sediment due to vertical mixing of the lake every year. Lake sediment should serve as annual PAHs repository. Detailed analyses of PAHs in core samples would reveal past annual fluxes of PAHs (pollution history by PAHs) and related human activities around the lake.

Conclusion

Seasonal deposition fluxes of PAHs are influenced by the size of the particles with which they are associated, and seasonal condition of the lake. In the vertical mixing period of the lake, deposition fluxes of (fine) aerosol particles are facilitated resulting in enhanced deposition fluxes of less volatile PAHs. Volatile PAHs are relatively enriched in (coarse) run off particles and their deposition fluxes are enhanced from summer to early autumn, especially in storm events. The contamination of oil-derived PAHs from water delivery equipments such as cruise ships, personal water crafts and ferries may also contribute deposition fluxes of volatile PAHs in this period. PAHs of any origin are entirely deposited due to vertical mixing of the lake every year. PAHs deposition fluxes of the North Basin of Lake Biwa is comparable to those in rural area in other locations.

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Table 1

Dates of installation and withdrawal of sediment trap.

Date
7/23 2003
8/19
9/25
10/21
11/20
12/18
1/20 2004
3/24
4/20
5/18
6/22
7/20

Table 2

Polycyclic Aromatic Hydrocarbons (PAHs) contents (ng g^{-1}) in sediment in remote/rural, mid size city, and urban/industrial area

Sampling site	Flu	Phe	Ant	BaA	Chr	BkF	BaP	BghiP	Total
Remote/rural									
Lake Biwa, sediment trap sample (this study)	43.9	541	21.4	42.2	53.3	25.1	25.1	51.6	780
Lake Biwa, surface sediment (this study)		11.7	11.9	14.4	20.6	12.2	25.1	39.6	140
High altitude lake, Europe[a]	8.7	50	2.0	14	59	64	23	72	7 200
Lake Michigan, USA[b]	7.10	210	36.8	162	348		268		
Mid size city									
Hyeongsan River, Korea[c]	46.0	130	32.0	130	190	150	250	190	2 200
Urban/industrial									
Kitimat Arm, UK[d]	789	8 000	1 630	12 900	10 500		17 500		171 000
Susquehanna River, USA[e]	226	967	331	427	489	194	629	416	9 850

[a] Fernández et al., 1999, one of the sampling sites., [b] Simcik et al., 1996, one of the sampling sites.,

[c] Koh et al., 2004, average of the samples., [d]Simpson et al., 1998, one of the samples for 180-38 um fraction.,

[e] Ko et al., 2007, one of averages

Table 3

PAHs fluxes (ng cm^{-2} $year^{-1}$) in remote/rural, mid size city, and urban/industrial area

Sampling site	Flu	Phe	Ant	BaA	Chr	BkF	BaP	BghiP	Total
Remote/rural									
Lake Biwa (this study)	4.10	47.9	2.10	4.30	5.80	2.60	26.0	5.20	75
Lake Suwa, Japan[a]									49
Lake Superior, USA[b]		0.40	0.01		0.80		0.20		
Mid size city									
Lake Windermere, UK[c]									470
Urban/industrial									
Pearl River, China[d]									More than 8 000
Narragansett Bay, USA[e]									9 500

[a] Ikenaka et al., 2005., [b] Gschwend and Hites, 1981, one of the sampling sites.,

[c]Cranwell and Koul, 1989, one of the sampling sites., [d] Bixian et al., 2001, [e]Latimer and Quinn, 1996, average of the samples.

Figure captions

Fig. 1

Geomorphological map of Lake Biwa and sampling location.

Fig. 2

Seasonal change in deposition fluxes of particles and precipitation amount.

Fig. 3

Seasonal change in mean particle size of sediment trap samples

Fig. 4

Scanning electron microscope (SEM) image of sediment trap samples collected in (a) October 2003 and (b) March 2004. Diatom cells are dominantly recognized in figure 4b while those are only sparsely recognized in figure 4a.

Fig. 5

Seasonal change in total organic carbon (TOC) (%) of sediment trap samples.

Fig. 6

Seasonal change in peak intensity ratio (mica/quartz) of sediment trap samples in X-ray diffraction (XRD) analyses.

Fig. 7

Seasonal change in deposition fluxes of Polycyclic Aromatic Hydrocarbons (PAHs)

Fig. 8

Seasonal change in Phenanthrene(Phe)/Anthracene(Ant) ratio of sediment trap samples.

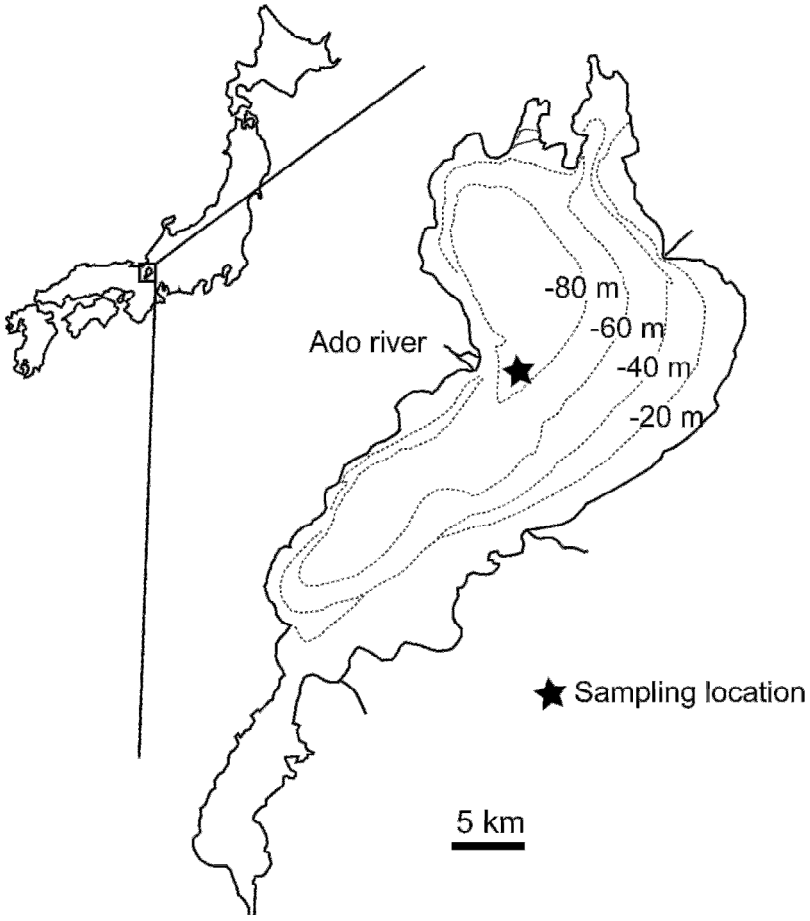

Figure 1

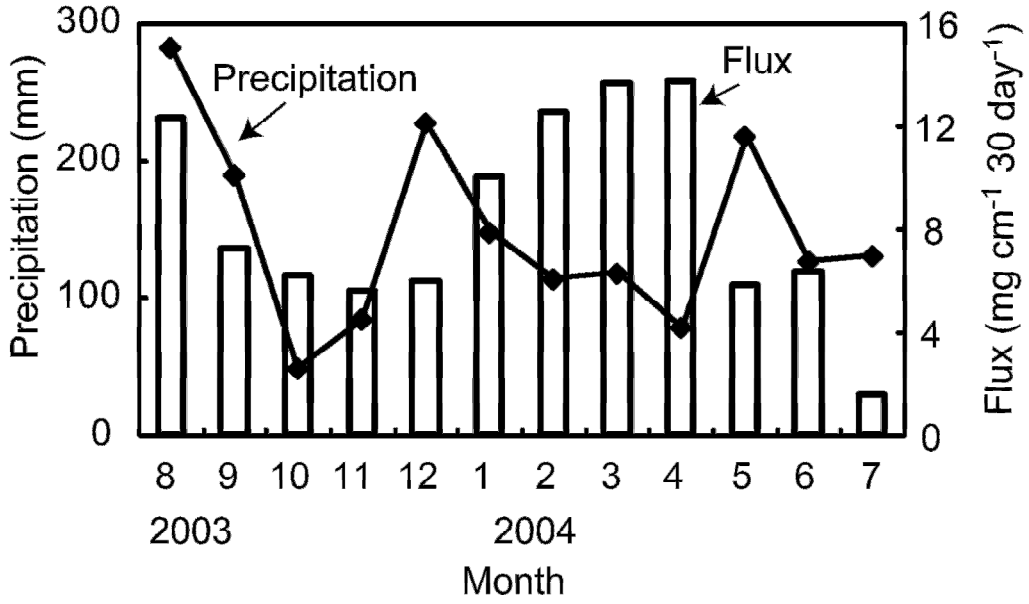
300
200
100
0
Precipitation (mm)
16
12
8
4
0
Flux (mg cm-1 30 day-1)
Precipitation
Flux
8 9 10 11 12 1 2 3 4 5 6 7
2003
2004
Month

Figure 2

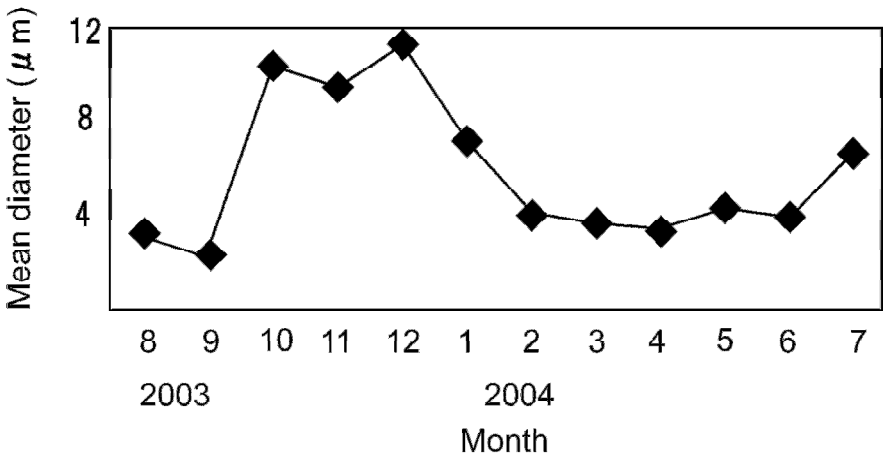

Figure 3

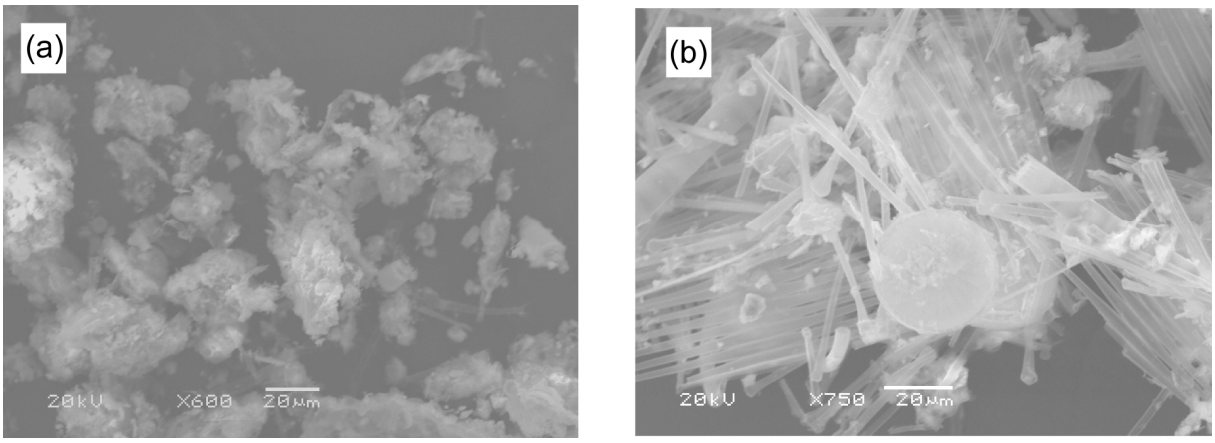

Figure 4

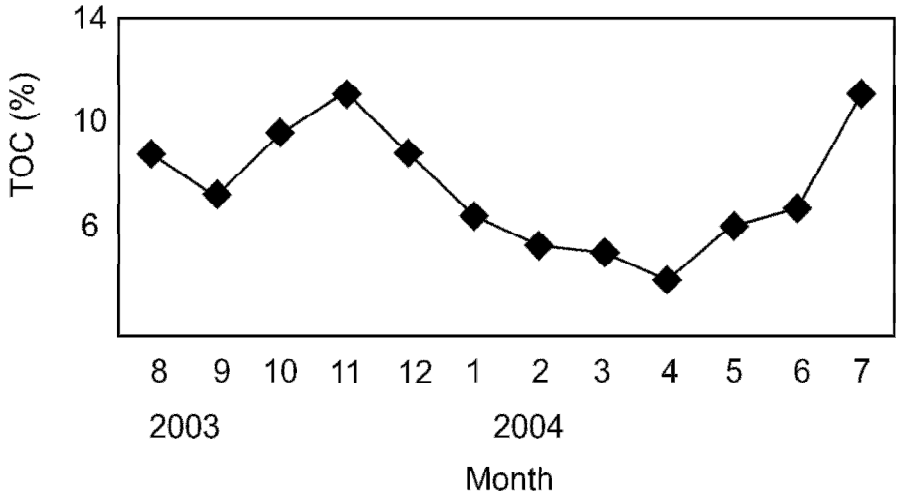

Figure 5

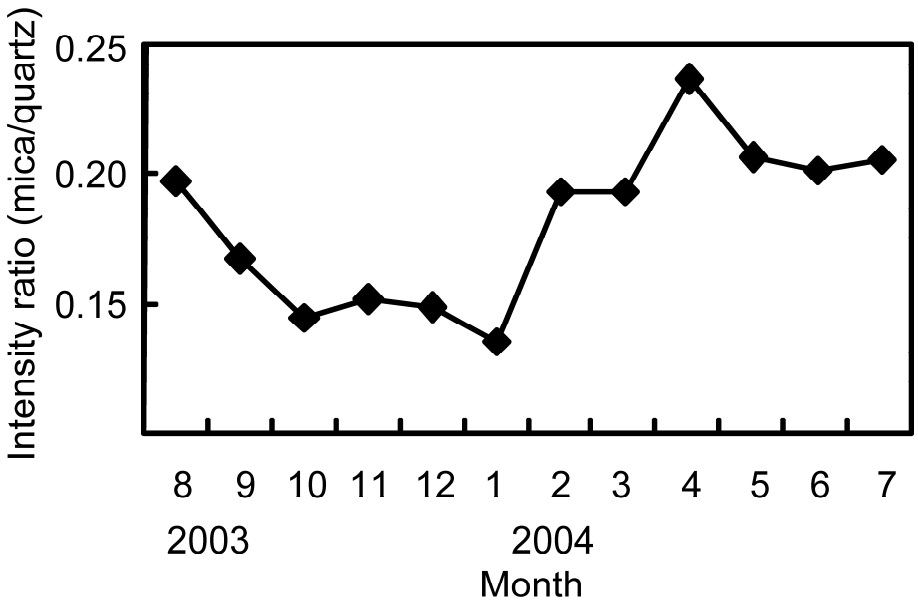
Intensity ratio (mica/quartz)
0.25
0.20
0.15
8
9
10
11
12
1
2
3
4
5
6
7
2003
2004
Month

Figure 6

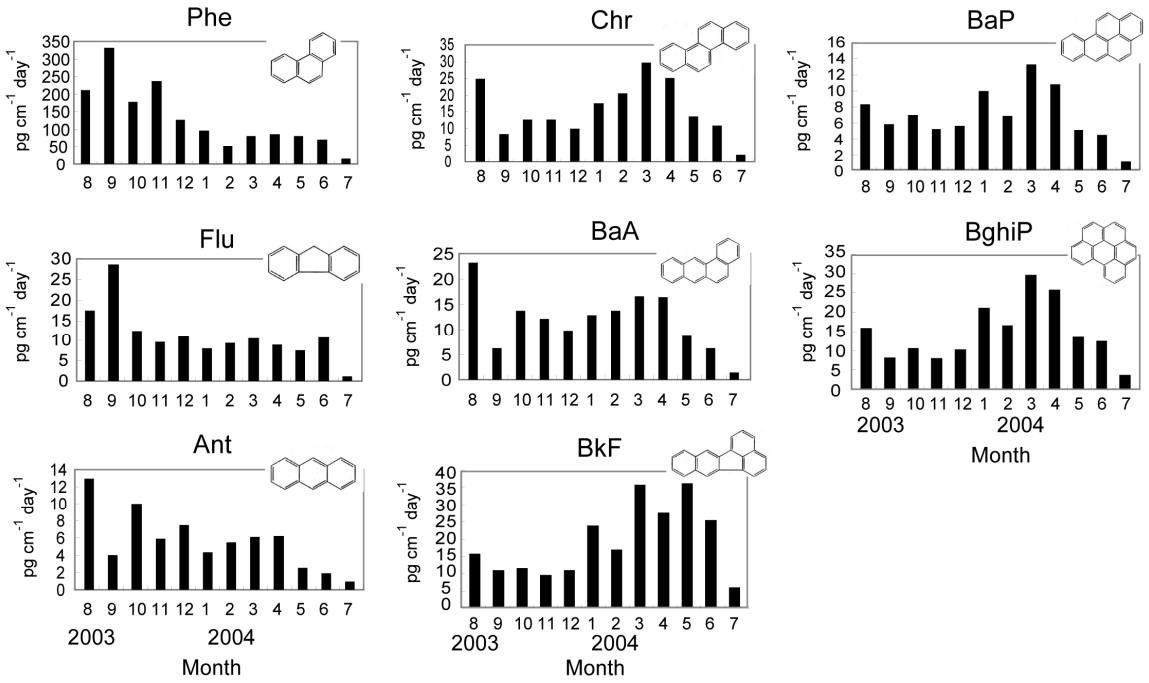
Phe
Chr
BaP
Flu
BaA
BghiP
Ant
BkF
pg cm-1 day-1
8 9 10 11 12 1 2 3 4 5 6 7
2003
2004
Month

Figure 7

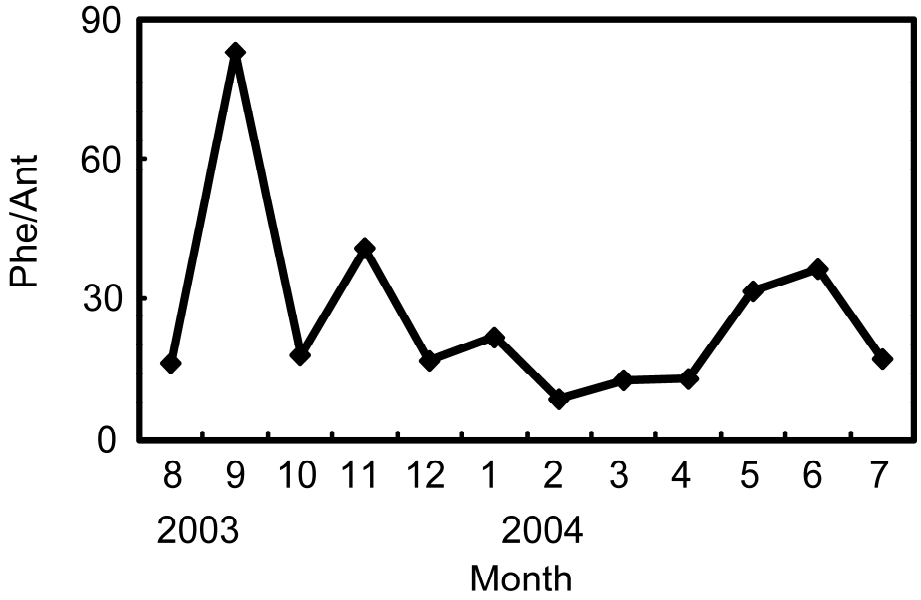

Figure 8